

PATENT SPECIFICATION

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(19)



(54) SELECTIVE HYDROGENATION PROCESS

(71) We, ENGELHARD MINERALS & CHEMICALS CORPORATION a corporation organized under the laws of the State of Delaware, United States of America, of 70 Wood Avenue South, Metro Park Plaza, Iselin, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

The present invention relates to the hydrogenation of unsaturated hydrocarbon compounds, and more particularly to the selective hydrogenation of one or more unsaturated compounds, or unsaturated portions of compounds contained in a feedstock. The use of selective hydrogenation of hydrocarbon compounds to prepare particular products and/or to confer desirable characteristics to various feedstocks is known throughout the oil and chemical industry. For example, selective hydrogenation is utilized to selectively remove olefins and diolefins from aromatic feedstocks to prevent the polymerization of these compounds, and hence avoid contamination of the products of later treatment of the feedstock. An example of this process is the hydrogenation of conjugated aliphatic or cyclic diolefins in naphtha streams that are blended into gasoline products or further processed for extraction of aromatic compounds.

Selective hydrogenation is also utilized to preferentially hydrogenate a portion or portions of hydrocarbon compounds while leaving unaltered other unsaturated portions of the same compound. For example, in the preparation of cumene (isopropylbenzene), alpha-methylstyrene is processed so as to hydrogenate the unsaturated aliphatic branch thereof without hydrogenating the aromatic benzene ring. Additionally, in those cumene production processes wherein the alpha-methylstyrene feedstock contains either naturally occurring or recycled cumene, ring saturation must obviously especially be avoided.

Catalysts and process conditions have been developed in this field to achieve the preferential hydrogenation required by the foregoing processes. Typically, catalysts containing supported noble metals such as platinum, palladium or ruthenium are utilized.

While the foregoing catalysts are generally effective in achieving an acceptable degree of hydrogenation specificity, improvement in this area is consistently sought. For example, it has been proposed to add certain organic nitrogen compounds to the feedstock in order to improve the selectivity of processes designed to produce cyclohexenes and substituted cyclohexenes by hydrogenation; see U.S. Patent No. 3,793,383.

Of particular concern in this area is the observation that catalyst selectivity in hydrogenation processes is poor when virgin or freshly regenerated catalysts are utilized, the selectivity gradually increasing as the catalyst ages on-stream. Thus, undesired aromatic ring hydrogenation occurs in the early stages of the process leading to product losses, the need for appropriate separatory equipment, and possible unsafe operation owing to potential temperature runaway situations due to the high activity of the catalyst. In the belief that the poor selectivity of fresh catalysts is attributable to rapid temperature rises at the start-up of the hydrogenation process, it has been proposed to place limits on the temperature and amount of hydrogen present at the start-up of the process; see U.S. Patent No. 3,769,358. There is a need, however, for further improvement in obtaining greater catalytic hydrogenation selectivity.

It is accordingly an object of this invention to develop an improved process for the selective hydrogenation of unsaturated hydrocarbon compounds.

A particular object of this invention is to improve the hydrogenation selectivity of hydrogenation catalysts, especially virgin or freshly regenerated hydrogen catalysts.

In accordance with this invention, the hydrogenation selectivity of catalysts, particularly virgin or freshly regenerated catalysts, is improved by a process comprising contacting a hydrogenation catalyst with gaseous ammonia for a period of time sufficient to increase the hydrogenation selectivity of the catalyst, and thereafter contacting the catalyst, in the presence of hydrogen, with a feedstock comprising either (a) at least one unsaturated compound for which hydrogenation is intended in the process and at least one unsaturated compound which is intended to remain unsaturated, or (b) a compound having a first unsaturated portion which is intended to be hydrogenated in the process, and a second unsaturated portion which is intended to remain unsaturated, or (c) a mixture of (b) and an unsaturated compound which is intended to remain unsaturated.

In a preferred embodiment of this invention, the contact of the catalyst with ammonia gas utilized in pre-treating the hydrogenation catalyst is continued during the hydrogenation process until the catalyst is found to have a suitable hydrogenation selectivity.

Exemplary feedstocks utilized in accordance with this invention include, respectively, (a) mixtures, such as naphtha, containing aromatics and mono- and diolefins, wherein hydrogenation of such olefins is desired without saturating the aromatic components of the feedstock or mixtures of, for example, acetylenes and diolefins; (b) alpha-methylstyrene wherein, in the conversion to cumene, it is desired to hydrogenate the unsaturated alkenyl side chain of the alpha-methylstyrene without hydrogenating the aromatic ring; and (c) a mixture of alpha-methylstyrene and cumene, wherein saturation of the alkenyl side chain of the alpha-methylstyrene is desired without causing saturation of the aromatic ring thereof or the aromatic ring of the cumene.

The process of this invention further comprises increasing the hydrogenation selectivity of a supported noble metal hydrogenation catalyst, which process comprises contacting the catalyst with ammonia in the vapor phase for a period of time sufficient to increase the hydrogenation selectivity of the catalyst. The catalyst may be contacted with the ammonia in the presence of a feedstock during a hydrogenation process or in the absence of a feedstock.

In accordance with more specific aspects of this invention, the catalysts utilized in the present process may be any of the well-known hydrogenation catalysts, generally comprised of a supported metal. Suitable metals include particularly the noble metals such as ruthenium, rhodium, palladium and platinum. Suitable supports include natural or treated clays such as kaolin or bentonite, siliceous materials, magnesium oxide, silica gel, alumina gel, natural or synthetic zeolites, and activated carbon and in suitable form, such as pellets, spheres, extrudates, and the like. Activated aluminas such as alpha-alumina, eta-alumina and gamma-alumina are especially useful supports. Preferred catalysts comprise platinum or palladium on alumina supports. When utilizing these or other noble metals on a support, the noble metal will typically be present in an amount from 0.01% to 5% by weight of the catalytic composition and preferably from 0.2% to 2.0% by weight.

The duration of time during which the hydrogenation catalyst is contacted with gaseous ammonia is not presently believed to be critical, it being noted that improved selectivity is noted after relatively short contact times, and continues to improve in a fairly regular manner as the duration of pre-treatment is extended. Where the presence of ammonia is continued with the flow of hydrocarbon feedstock and hydrogen after pre-treatment, the duration of pre-treatment needed to obtain improved selectivity will generally be shorter than in the case where the presence of ammonia is terminated upon introduction of the feedstock and hydrogen. As will be apparent to those skilled in this art, practical considerations such as economics may dictate the extent of pretreatment, e.g., the degree of improvement in selectivity achieved for each increase in the duration of pretreatment may at some point become so small as to not warrant any longer periods of pretreatment.

The pretreatment of the hydrogenation catalyst with ammonia may conveniently be carried out in the hydrogenation reaction vessel. The pretreatment may consist either of continuously flowing ammonia over the catalyst or admitting a predetermined amount of ammonia to the reaction vessel which is thereafter closed off to maintain contact between the catalyst and ammonia. The conditions utilized during this pretreatment may vary widely, subject to the provision that the ammonia be maintained in the gaseous state. Typical temperatures may range from 20°C to 200°C, preferably 100°C to 150°C, and pressures from 30 psig. to 400 psig. The amount of ammonia vapor contacted with the hydrogenation catalyst may vary widely depending upon the feedstock to be hydrogenated, the degree of selectivity required and other like factors. The ammonia may be contacted with the catalyst as pure ammonia vapor or alternatively admixed with a suitable gas such as nitrogen, helium, hydrogen and the like.

In a preferred embodiment of this invention, contact of the hydrogenation catalyst with

ammonia is maintained during the hydrogenation reaction, i.e., along with the mixture of feedstock and hydrogen. Thus, following a predetermined duration of pretreatment in the absence of feedstock and hydrogen, the hydrogenation reaction is commenced by introduction of the feedstock and hydrogen and ammonia vapor. While the ammonia vapor may be introduced as a separate feed stream or as part of the hydrocarbon feedstock, it is preferred to admit it to the reaction vessel in the hydrogen stream. When so doing, the ammonia is maintained in an amount from 0.15 to 20% by volume of the hydrogen stream. For typical hydrogen to hydrocarbon molar ratios employed in selective hydrogenation, the ammonia is generally present in an amount from 0.01% to 2.0% by weight based on the liquid feed. It has been found that this ammonia feed during hydrogenation may be terminated at such time that it appears that the desired degree of selectivity is achieved.

Once the desired degree of pretreatment, i.e., the contact of the catalyst with ammonia, is completed, hydrogenation proceeds according to well-known procedures. The conditions at which such selectivity hydrogenation is conducted will, of course, vary depending upon the feedstock to be treated and the hydrogenation desired, but typical processes utilize temperatures from 60°C to 200°C, pressures from 80psig. to 1500psig., and liquid hourly space velocities from 0.25 to 40. The feedstock to be hydrogenated is maintained in the liquid phase and the molar ratio of hydrogen to the unsaturated hydrocarbon to be hydrogenated in the feedstock may be from 1:1 to 5:1.

As earlier noted, the hydrogenation reaction is preferably conducted in the presence of gaseous ammonia.

According to a specific embodiment of the present invention, alpha-methylstyrene is converted to cumene by contacting a noble metal catalyst with ammonia vapor in the absence of hydrocarbon feedstock and hydrogen, and thereafter introducing hydrogen along with the feedstock to selectively hydrogenate the aliphatic portion of the alpha-methylstyrene without causing hydrogenation of the aromatic ring.

The following examples are presented to illustrate the process of the present invention.

EXAMPLE I

To a reaction vessel containing a catalyst composition comprised of 0.3 wt. % palladium on 1/8 inch diameter cylindrical alumina pellets was added 100% ammonia vapor at 50 psig. The vessel was closed off and contact of the ammonia with the catalyst was maintained at room temperature for 2 hours. The ammonia was then heated to 140°C and contact continued with the catalyst at this temperature for an additional 2 hours. Thereafter, the vessel was cooled and vented.

A feedstock of the following composition

Alpha-methylstyrene	19.8% by weight	
Hydroxyacetone	280 p.p.m.	
Benzofuran	110 p.p.m.	
Cumene	Balance	

was passed over the pretreated catalyst with hydrogen at 100 psig., a temperature of 80°C, a liquid hourly space velocity of 2.0 (lbs feed/lb. catalyst/hr.), and a hydrogen to alpha-methylstyrene mole ratio of about 3.0.

Table I summarizes the results of this hydrogenation process. The effectiveness of the catalyst selectivity is monitored by measurement of the production of isopropyl cyclohexane which indicates that hydrogenation of both the alkenyl group and the aromatic ring structure has occurred. Despite the decrease in hydrogenation of alpha-methylstyrene to isopropyl cyclohexane, the hydrogenation to cumene remains high, indicating that selectivity of the catalyst is improving.

TABLE I

	Hours on Stream (after pretreatment)	IPCH ¹ in Product wt. percent	AMS ² in Product wt. percent	
5	0.3	0.0353	0.71	5
	1.8	0.0296	0.12	
10	1.3	0.0286	0.06	10
	1.8	0.0345	0.05	
	2.3	0.0373	0.04	
15	2.8	0.0232	0.03	15
	3.3	0.0290	0.03	
20	4.8	0.0235	0.03	20
	21.8	0.0090	0.12	
	24.5	0.0039	0.14	
25	28.3	0.0027	0.13	25
	1 Isopropyl cyclohexane			
30	2 Alpha-methylstyrene			30

EXAMPLE II

Utilizing fresh catalyst sample of the same composition employed in Example I, 100% ammonia was contacted with the catalyst in a closed reaction vessel at room temperature and 90 psig. for two hours. The vessel was then vented and the catalyst utilized for selective hydrogenation of alpha-methylstyrene employing the same feed conditions described in Example I with the exception that ammonia vapor was added with the hydrogen stream (10% by volume of hydrogen stream; approximately 0.9% by weight of liquid feed). The results are summarized in Table II.

TABLE II

	Hours on Stream (after pretreatment)	IPCH in Product wt. percent	AMS in Product wt. percent	
45	0.6	0.0380	.56	45
	1.2	0.0220	.48	
50	1.6	0.0100	1.31	50
	2.1	0.0030	2.22	
55	2.6	< 0.0030	2.89	55
	3.1	< 0.0030	3.36	

EXAMPLE III (for comparison)

Over a fresh catalyst sample of the same composition as utilized in the previous examples was passed hydrogen and a feedstock having a composition similar to that in the previous examples (21% alpha-methylstyrene) at a temperature of 80°C, a pressure of 100 psig., a liquid weight hourly space velocity of 2.0 and a hydrogen to AMS mole ratio of 3.5. No pretreatment with ammonia was provided.

The results of this run are summarized in Table III.

TABLE III

5	Hours on Stream	IPCH in Product wt. percent	AMS in Product wt. percent	5
	.8	0.1820	0.07	
10	1.3	0.1560	0.03	10
	1.8	0.1450	0.02	
	2.3	0.1280	0.02	
15	2.8	0.1260	0.02	15
	3.8	0.1240	0.01	
20	20.6	0.0750	0.02	20
	23.3	0.0660	<.01	
	25.8	0.0610	<.01	
25	28.3	0.0550	<.01	25
	44.6	0.0130	<.01	
30	45.6	0.0110	<.01	30

It will be noted comparing Tables I and III that the pretreatment according to the invention has reduced the production of isopropyl cyclohexane substantially while not affecting the hydrogenation of alpha-methylstyrene.

35 When expressed in terms of the duration of hydrogenation reaction elapsed for the level of isopropyl cyclohexane in the product stream to decrease to 100 p.p.m., the process of Example I required about 16 hours; Example II about 2 hours; and Example III about 50-60 hours. Both Examples of the process of the invention (I and II) significantly decrease the time period when off-specification product is made, since in this application of the invention isopropyl cyclohexane is undesirable and must be kept at a low concentration.

40 The overall effect of a preferred ammonia pretreatment method is seen in a high ratio of the rate constant for disappearance of alpha-methylstyrene to the rate constant for appearance of isopropyl-cyclohexane. This ratio defines the selectivity of the catalyst and is calculated as follows. The rates of the two reactions can be expressed as:

$$\text{Rate of disappearance of AMS} = - \frac{dC_{\text{AMS}}}{dt} = k_{\text{AMS}} C_{\text{AMS}} \quad (1)$$

$$\text{Rate of appearance of IPCH} = \frac{dC_{\text{IPCH}}}{dt} = k_{\text{IPCH}} \quad (2)$$

Where,

k_{AMS} = AMS Rate constant, $1/\text{time}$
 k_{IPCH} = IPCH Rate constant, $\text{Mol \%}/(\text{time})$
 C = Component concentration, mol \%
 t = Residence time, hrs.

The above expressions must be integrated to calculate the rate constants from the data listed in the Examples, obtaining:

$$k_{\text{AMS}} = \frac{1}{t} \ln \frac{C_{\text{AMS}}(\text{in})}{C_{\text{AMS}}(\text{out})} \quad (3)$$

$$k_{\text{IPCH}} = \frac{1}{t} [C_{\text{IPCH}}(\text{out}) - C_{\text{IPCH}}(\text{in})] = \frac{1}{t} C_{\text{IPCH}}(\text{out}) \quad (4)$$

The selectivity is then conveniently expressed as $k_{\text{AMS}}/k_{\text{IPCH}}$ by dividing Eq (3) by Eq (4):

$$\frac{k_{\text{AMS}}}{k_{\text{IPCH}}} = \frac{\ln \frac{C_{\text{AMS}}(\text{in})}{C_{\text{AMS}}(\text{out})}}{C_{\text{IPCH}}(\text{out})} \quad (5)$$

The selectivities calculated for Examples I and III are shown in Figure 1. It can be seen that the pretreated catalyst of Example I is significantly better than the untreated catalyst of Example III during the first hours of operation. The pretreated catalyst produces less IPCH than the untreated catalyst while hydrogenating substantially all the AMS present. Although the selectivity of the catalyst when the hydrogenation reaction begins is nearly the same for both Example I and III, the selectivity of the catalyst pretreated with ammonia, Example I, improves rapidly and has a clear advantage over the untreated catalyst of Example III. If Example II were plotted on the same graph, it would be expected to appear as a curve lying above that of Example I since a catalyst pretreated with ammonia and then contacted with ammonia during hydrogenation has even more rapid increase in selectivity than when the catalyst is only pretreated.

WHAT WE CLAIM IS:

1. A process for increasing the efficiency of selective hydrogenation catalysts during start-up periods which comprises initially contacting the catalyst with ammonia vapor; and then contacting the thus-treated catalyst with hydrogen and a feedstock in liquid phase under hydrogenation conditions, which feedstock comprises (a) at least one unsaturated compound for which hydrogenation is intended in the process and at least one unsaturated compound which is intended to remain unsaturated, or (b) a compound having a first unsaturated portion which is intended to be hydrogenated in the process, and a second unsaturated portion which is intended to remain unsaturated; or (c) a mixture of (b) and an unsaturated compound which is intended to remain unsaturated.

2. A process as claimed in Claim 1 wherein the catalyst to be treated is directed to the selective hydrogenation of aromatic compounds having one or more unsaturated ring substituents to obtain a product comprising aromatic compounds having one or more saturated ring substituents.

3. A process as claimed in Claim 2 wherein a noble metal catalyst is utilized and treated with ammonia, and the feedstock contains alpha-methylstyrene and cumene in the presence of hydrogen under hydrogenation conditions.

4. A process as claimed in any preceding Claim wherein said contacting with gaseous

ammonia is at a temperature of from 20°C to 200°C and a pressure of from 30 psig. to 400 psig.

5. A process as claimed in any preceding Claim wherein the contact of said catalyst with gaseous ammonia is continued along with the contact of feedstock and hydrogen with said catalyst. 5
6. A process as claimed in Claim 5 wherein said continued contact with ammonia comprises admixing ammonia with said hydrogen.
7. A process as claimed in Claim 6 wherein said ammonia is present in an amount of from 0.15% to 20% by volume of said hydrogen.
- 10 8. A process as claimed in any of Claims 1 and 4 to 7 wherein said compound, in said feedstock, intended to be hydrogenated is an unsaturated aliphatic compound, and said feedstock also comprises aromatic compounds intended to remain unsaturated. 10
9. A process as claimed in any preceding Claim wherein said feedstock and hydrogen are contacted with said catalyst at a temperature of from 60°C to 200°C., a pressure of from 80 psig. to 1500 psig., and a mol ratio of hydrogen to unsaturated hydrocarbon to be hydrogenated of from 1:1 to 5:1. 15
10. A process as claimed in any preceding Claim wherein said hydrogenation catalyst comprises palladium, platinum or a mixture thereof.
11. A process as claimed in Claim 1 and substantially as hereinbefore described with reference to Example I or II. 20

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AGENTS FOR THE APPLICANTS

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COMPLETE SPECIFICATION

1 SHEET

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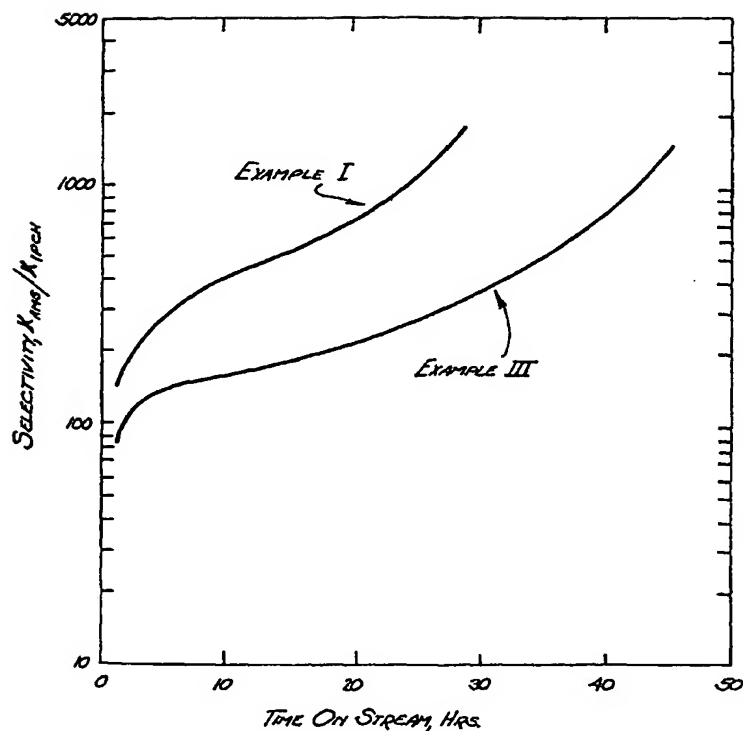


Fig. 1.
PROCESS SELECTIVITY